

Nanostructured Design of Sulfur Cathode for High-Energy Lithium-Sulfur Batteries

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Project ID
bat230

Overview

Timeline

- Start: October 1, 2017
- End: Sep 30, 2020
- Percent complete: 90%

Budget

- Total project funding
\$1050k from DOE
- Funding for FY19
\$300k
- Funding for FY20
\$450k

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

**Targets: cost-effective and high-energy
electrode materials and batteries**

Partners

- Collaboration
 - BMR program PI's
 - SLAC: In-situ X-ray, Mike Toney
 - Prof. Steven Chu, Stanford
 - Prof. Zhenan Bao, Stanford
 - PNNL scientists: Jun Liu, Jie Xiao

Project Objective and Relevance

Objective

- Develop lithium-sulfur batteries to power electric vehicles (HEV/PEV/EV) and decrease the high cost of batteries.
- Develop sulfur cathodes with high capacity and stability to generate high energy lithium-sulfur batteries with long cycle life.
- Design and fabricate novel nanostructured sulfur cathode with multifunctional coatings to overcome the materials challenges that lead to short battery life, including volume expansion, active material loss and low conductivity of sulfur cathode.
- Develop scalable low-cost methods for the synthesis of nanostructured sulfur cathode.
- Project contents are directly aimed at the listed barriers: high cost, low energy density and short battery life.

Milestones for FY19 and 20

Month/year	Milestones
1/2019	Develop a non-invasive imaging method with sub-micron, sub-second resolution for Li-S battery in label-free, native organic liquid electrolyte (completed)
4/2019	Demonstrate the substrate-dependent electrochemical formation of super-cooled liquid sulfur and crystals, as well as rapid solidification of a super-cooled sulfur droplet (completed)
7/2019	Provide direct evidence about a long-debated reaction pathway of surface mechanism vs. solution mechanism for sulfur and the current collector effect on sulfur evolution (completed)
10/2019	Investigate the sulfur growth behaviors on different current collectors and correlate the results with their electrochemical performance (completed)
1/2020	Design and fabrication of $\text{Li}_2\text{S}@$ TMDs cathodes for high-energy all-solid-state Li-S battery (completed)
4/2020	In-operando optical imaging of the polysulfide shuttling in all-solid-state Li-S battery (On track)

Approach/Strategy

Advanced nanostructured sulfur cathodes design and synthesis

- 1) Engineer empty space into sulfur cathode to solve the problem of electrode volume expansion.
- 2) Develop novel sulfur nanostructures with multi-functional coatings for the confinement of sulfur/lithium polysulfides to address the issues of active materials loss and low conductivity.
- 3) Develop/discover optimal nanostructured materials that can capture the polysulfide dissolved in the electrolyte.
- 4) Develop space efficiently packed nanostructured sulfur cathode to increase the volumetric energy density and rate capability.
- 5) Identify the interaction mechanism between sulfur species and different types of oxides/sulfides, and find the optimal material to improve the capacity and cycling of sulfur cathode.

Structure and property characterization

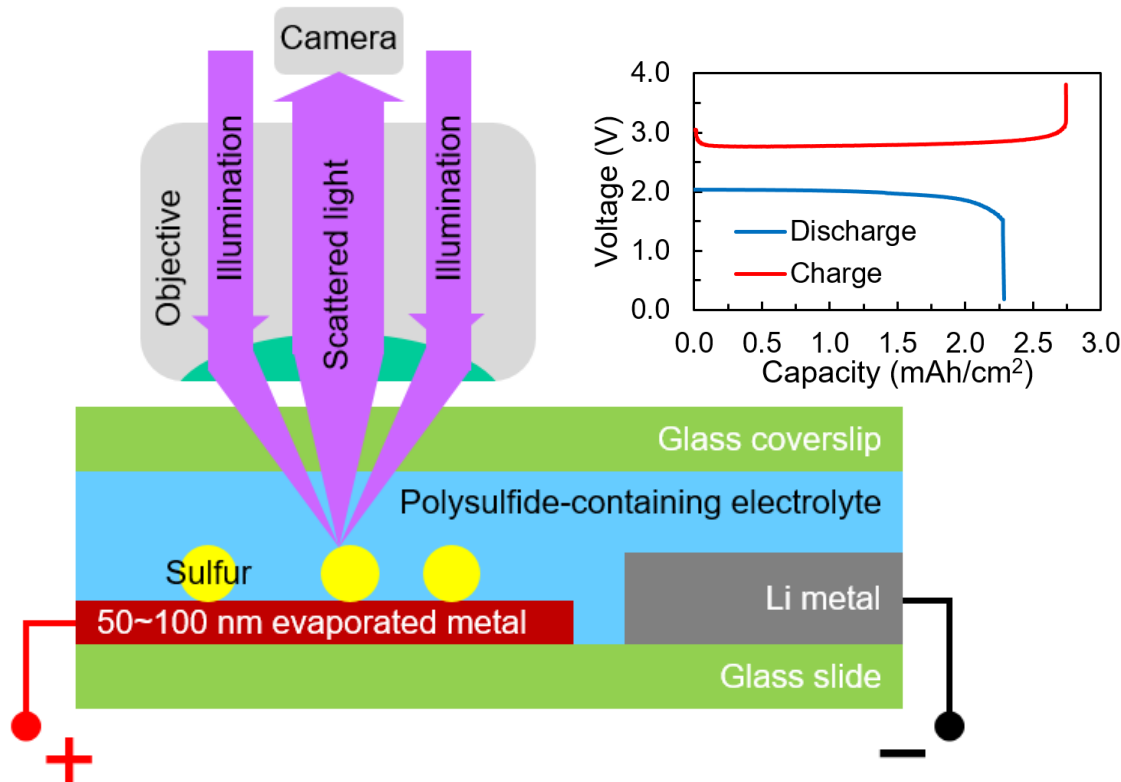
- 1) Ex-situ transmission electron microscopy
- 2) Ex-situ scanning electron microscopy
- 3) Inductively Coupled Plasma elemental analysis
- 4) In operando X-ray diffraction and transmission X-ray microscopy

Electrochemical testing

- 1) Coin cells and pouch cells
- 2) A set of electrochemical techniques

Accomplishment

Transparent Li-S cell for light microscopy



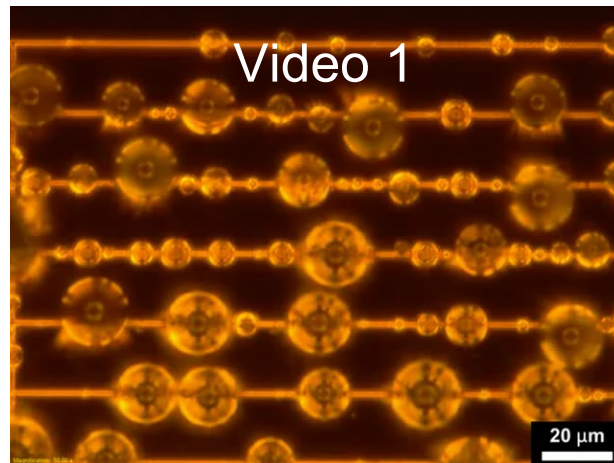
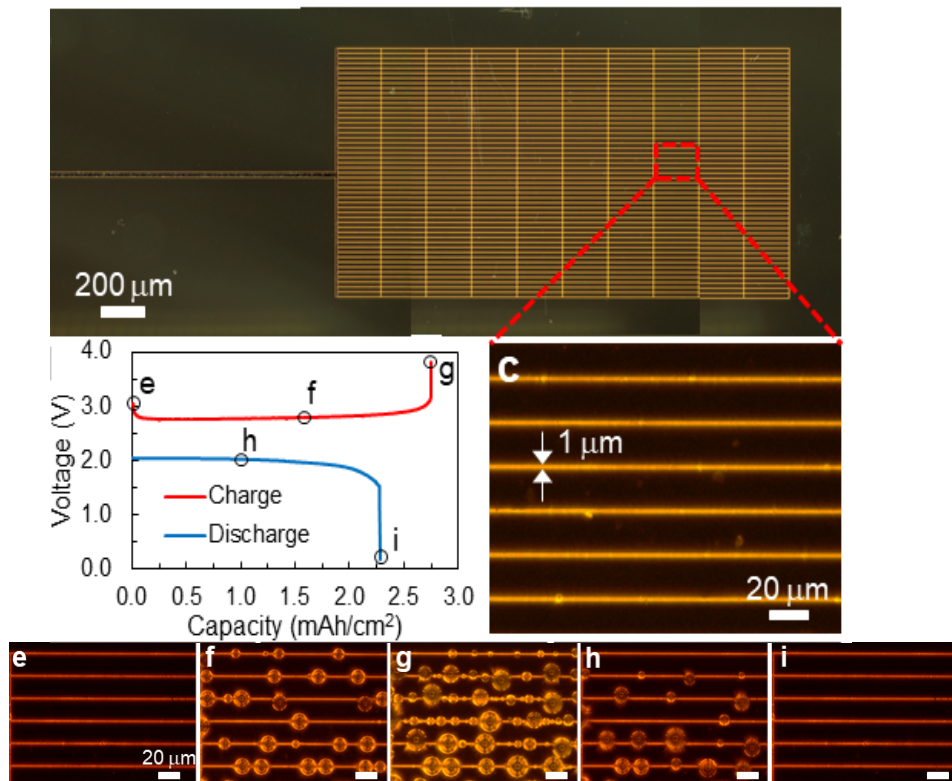
Probing sulfur electrochemistry challenges:

- Sulfur species are sensitive to vacuum, electron beam irradiation and X-ray irradiation, which limits the diagnostic tools;
- Sulfur has multiple reaction pathways, which could be easily disturbed by added indicators or labels;
- The materials easily change upon removing from native electrolyte, hence requiring *in operando* study.

Cui group, PNAS, 116, 765 (2019)

Accomplishment

Transparent Li-S cell for light microscopy

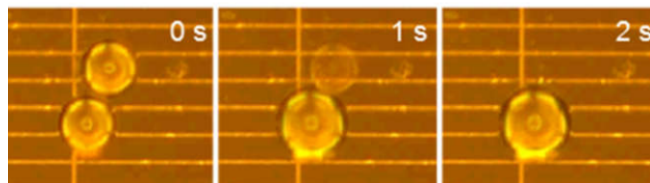
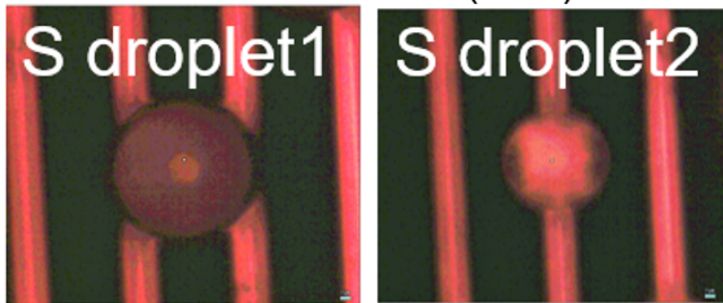
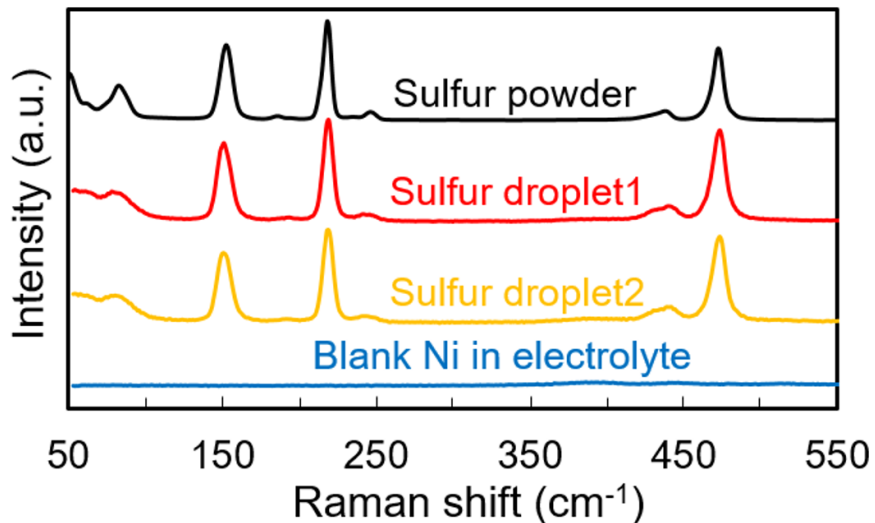


Cyclo-S₈
Melting point:
115.2°C

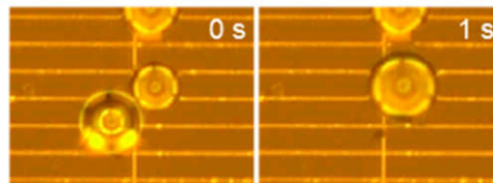
Cui group, PNAS, 116, 765 (2019)

Accomplishment

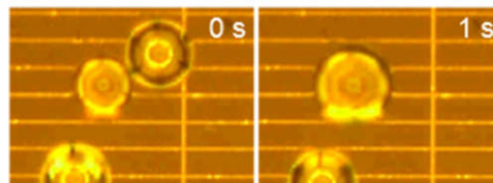
Raman spectra of these droplets



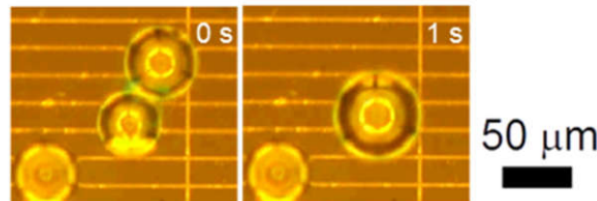
Upper: 37 μm
Lower: 37 μm
Sum: 47 μm
Merge: 48 μm



Left: 44 μm
Right: 31 μm
Sum: 49 μm
Merge: 47 μm



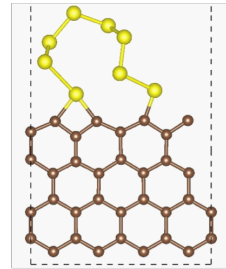
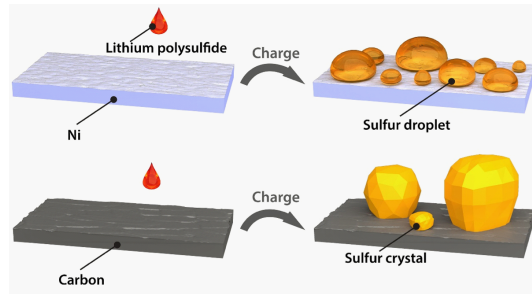
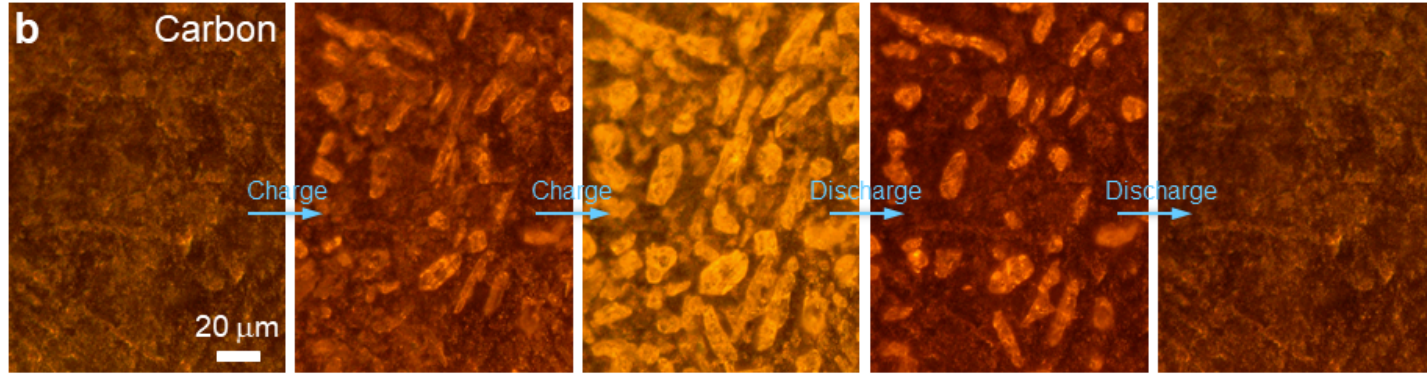
Left: 41 μm
Right: 45 μm
Sum: 54 μm
Merge: 55 μm



Upper: 50 μm
Lower: 44 μm
Sum: 59 μm
Merge: 60 μm

Accomplishment

Sulfur crystal formation on carbon



Graphene Zigzag edge

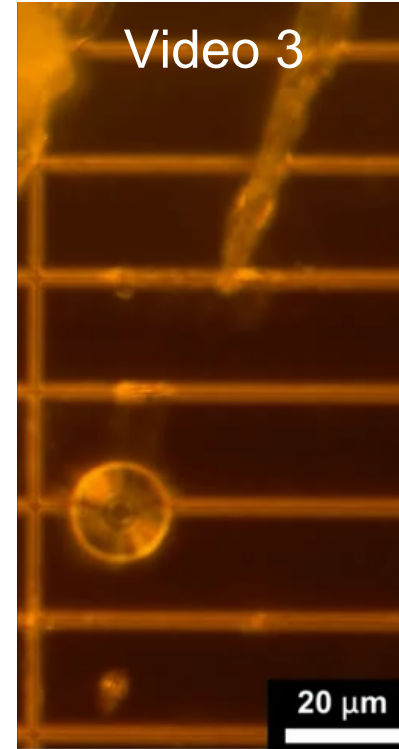
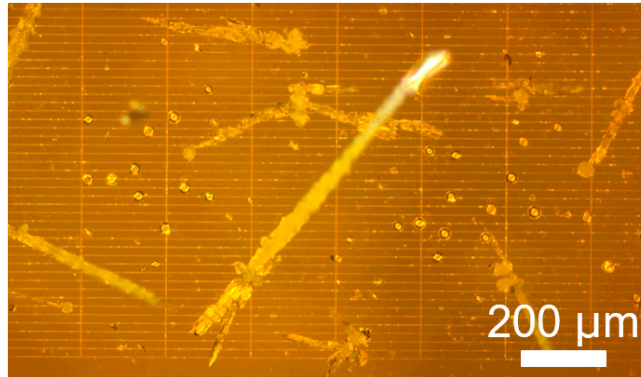
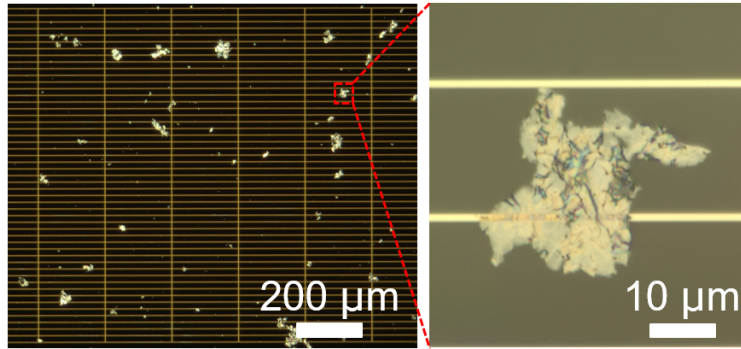
$$E_{\text{ad}} = -3.21 \text{ eV}$$



Cui group, PNAS, 116, 765 (2019)

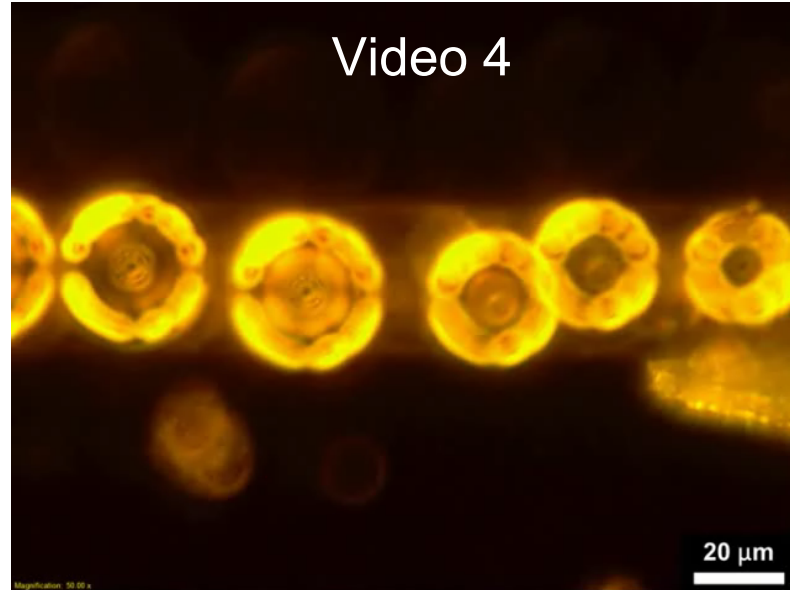
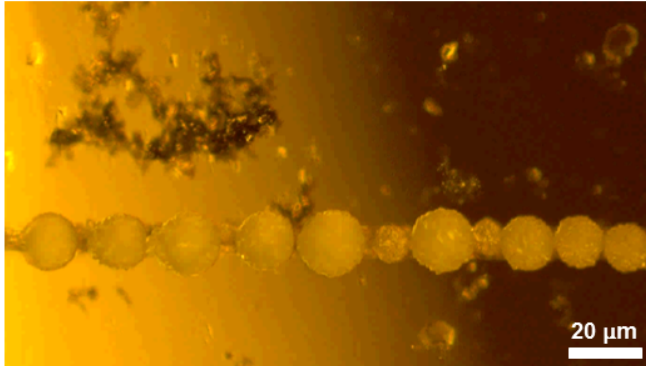
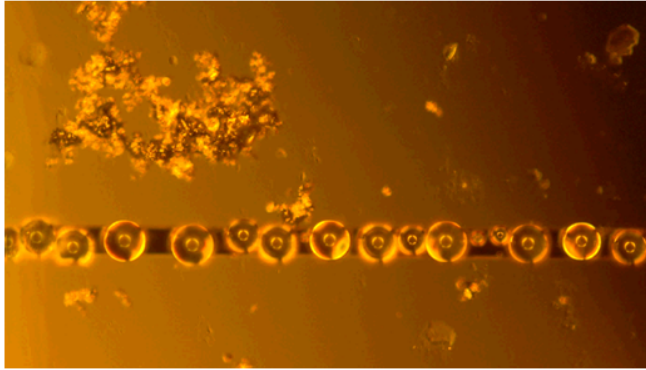
Accomplishment

Rapid solidification of super-cooled liquid sulfur



Accomplishment

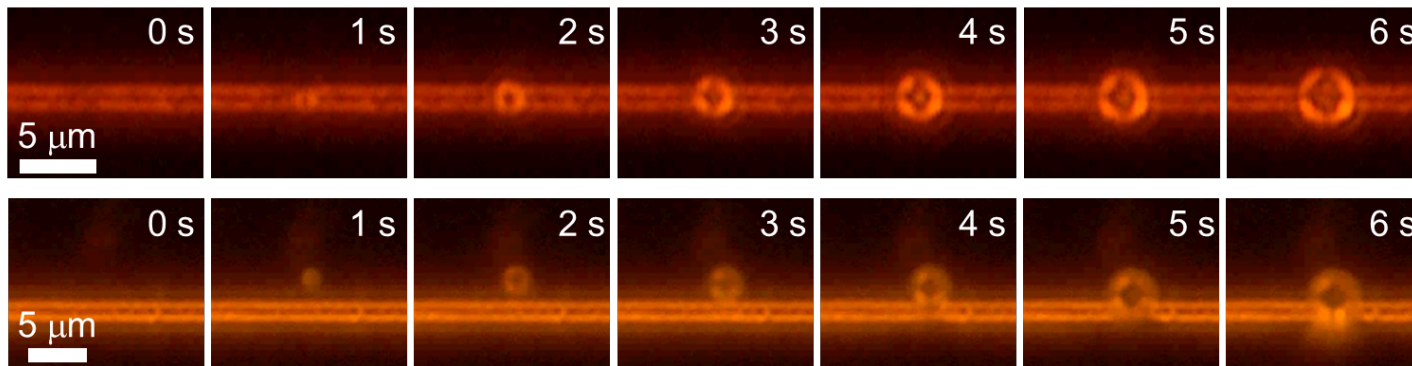
Rapid solidification of super-cooled liquid sulfur



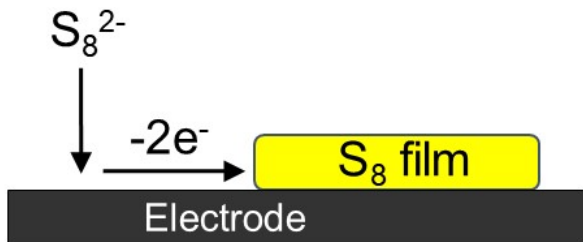
Cui group, PNAS, 116, 765 (2019)

Accomplishment

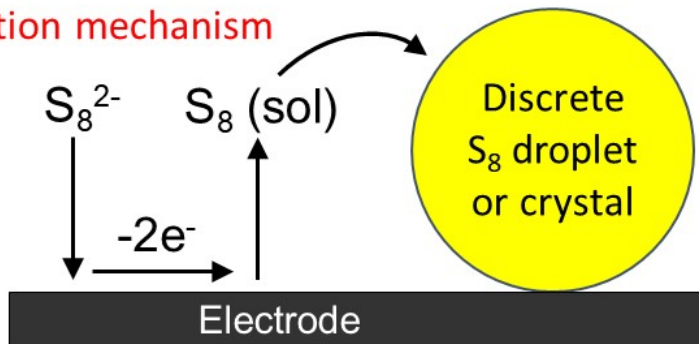
Surface or solution mechanism in Li-S batteries?



Surface mechanism

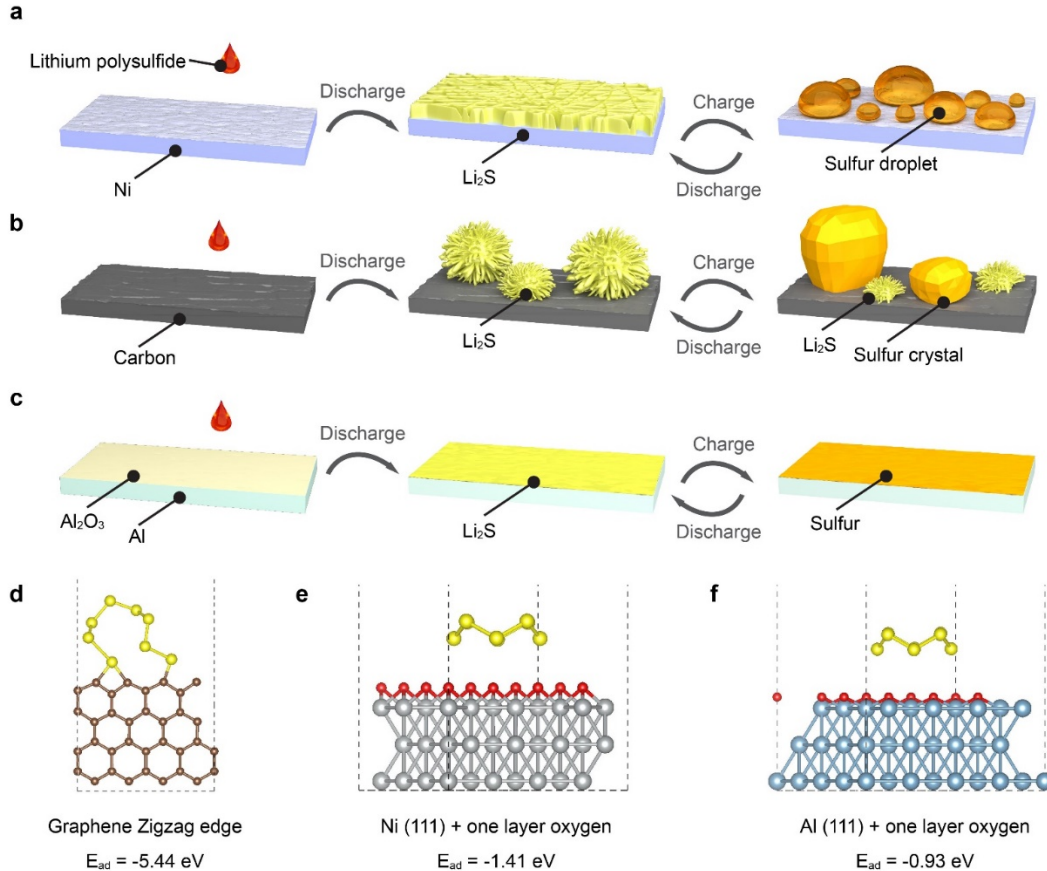


Solution mechanism

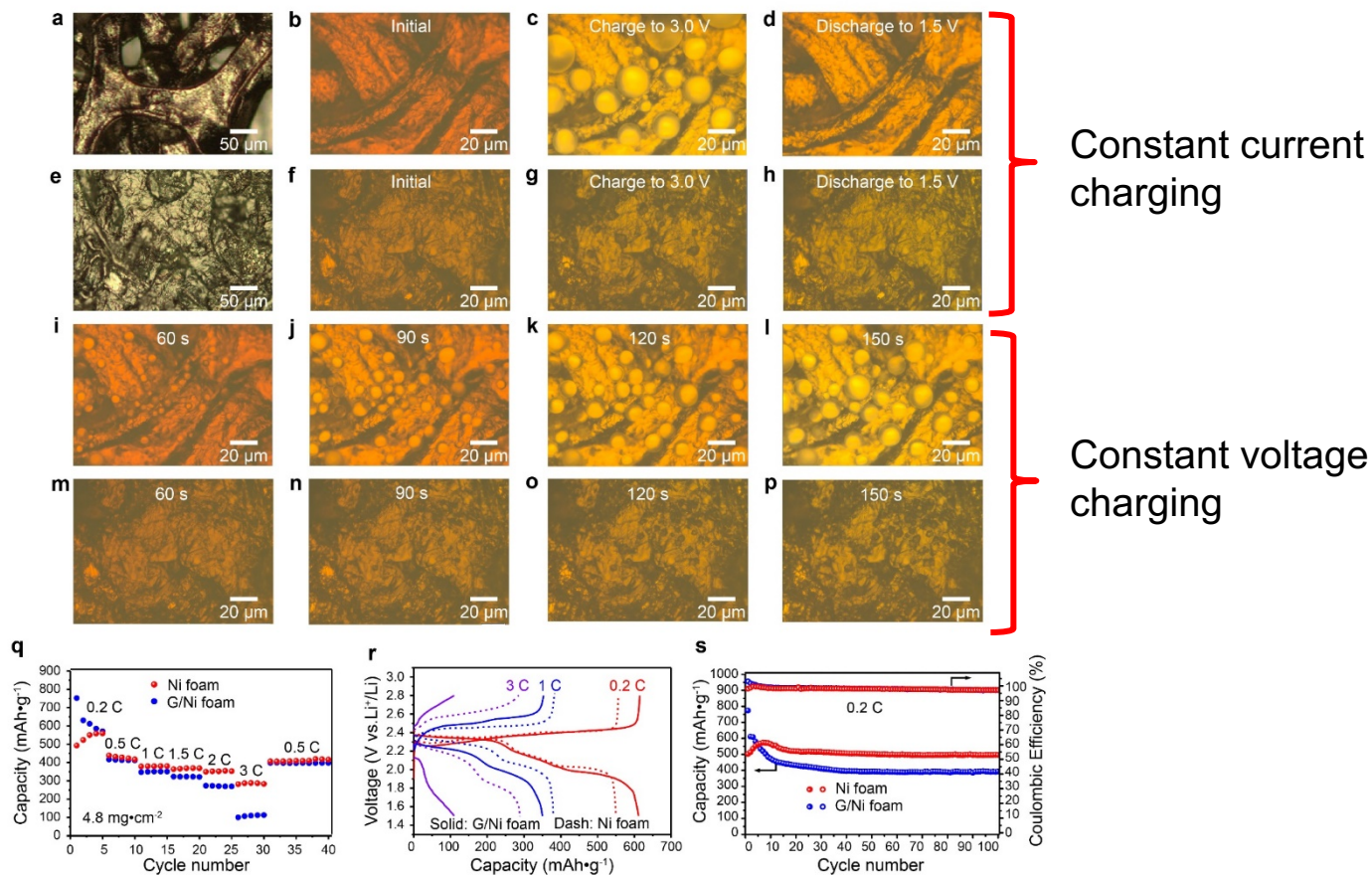


Cui group, PNAS, 116, 765 (2019)

Accomplishment



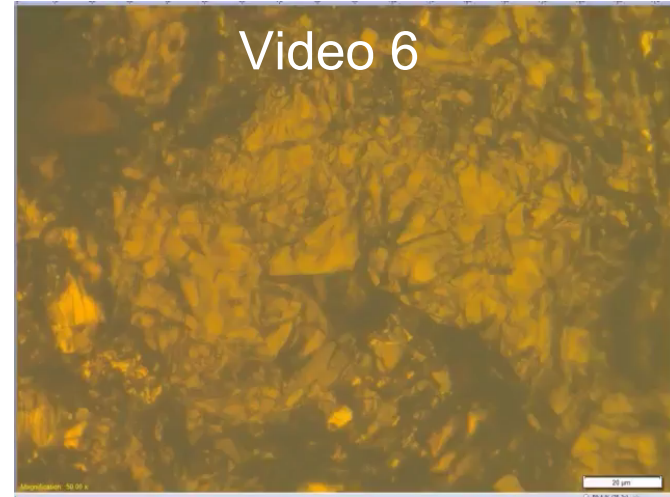
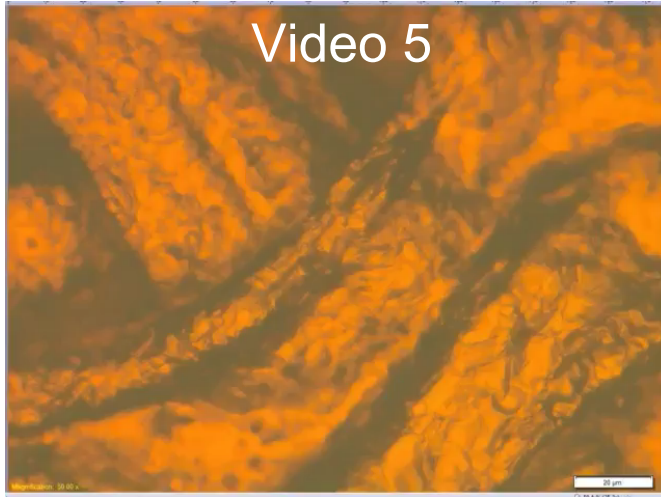
Accomplishment



Cui group, *Sci Adv.*, in press (2020)

Accomplishment

Observation of sulfur growth on Ni and G/Ni foam

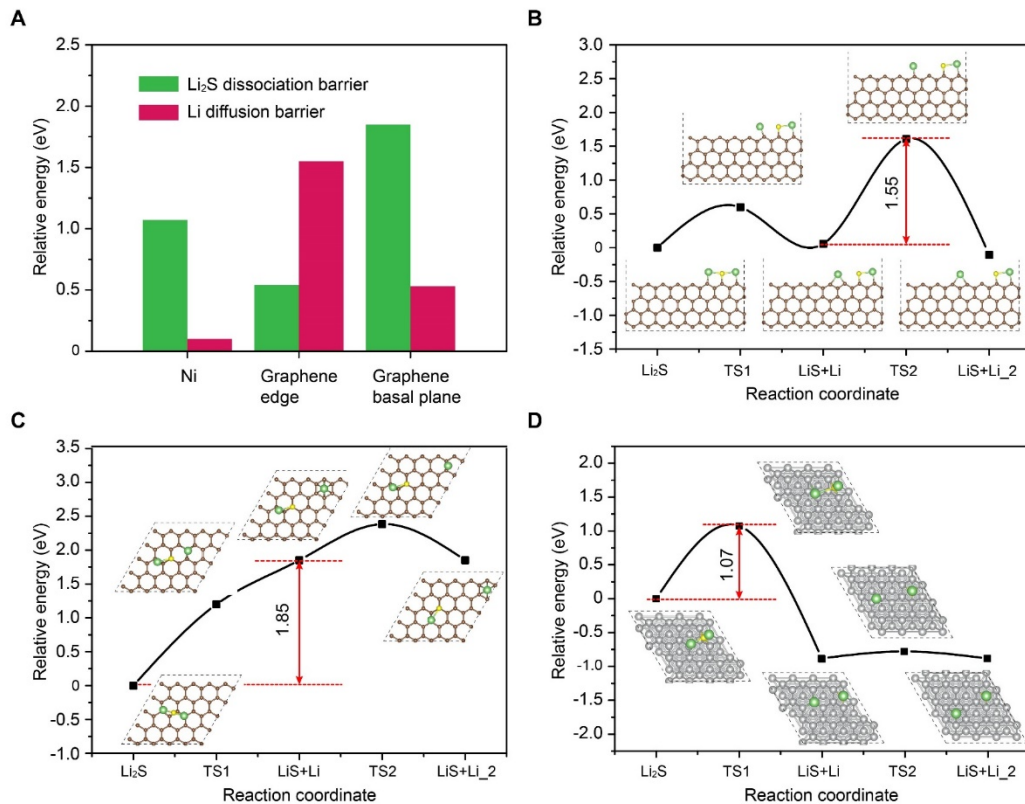


The electrochemical cell was constantly voltage charged at 3.5 V.

Cui group, Sci Adv., in press (2020)

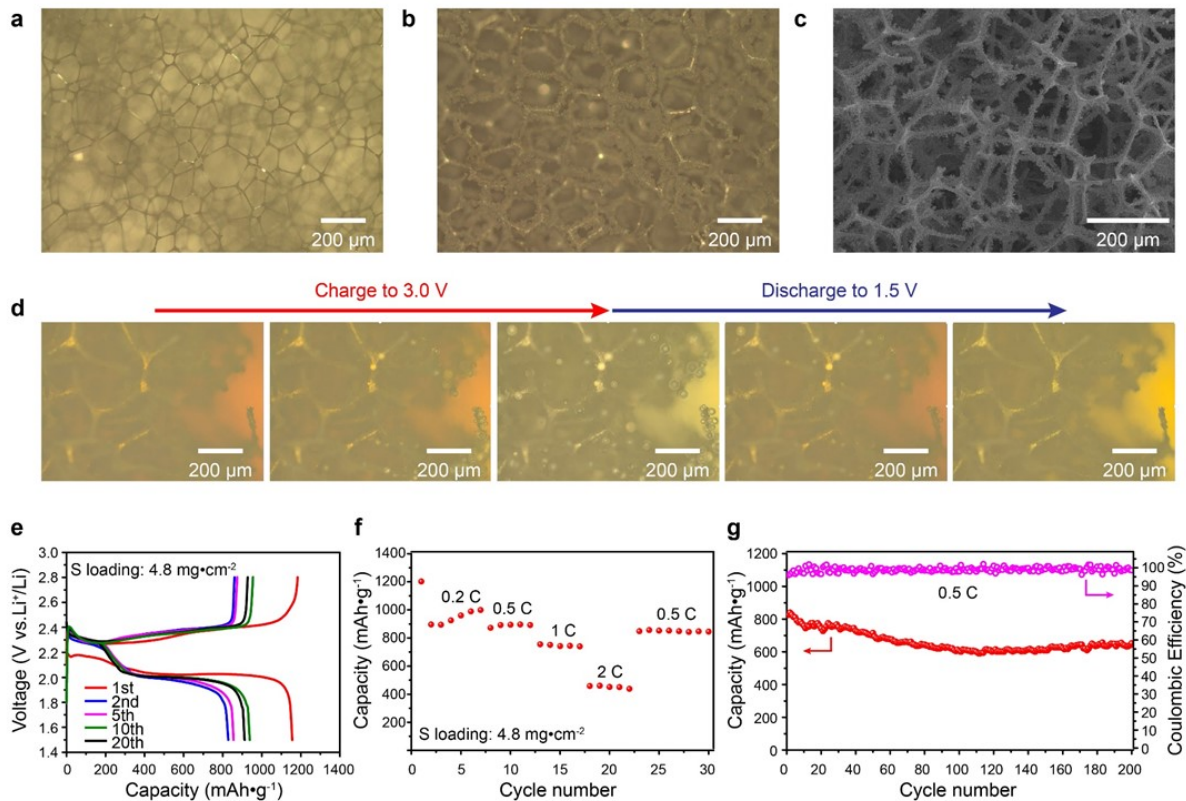
Accomplishment

Li₂S decomposition and Li ion diffusion barriers



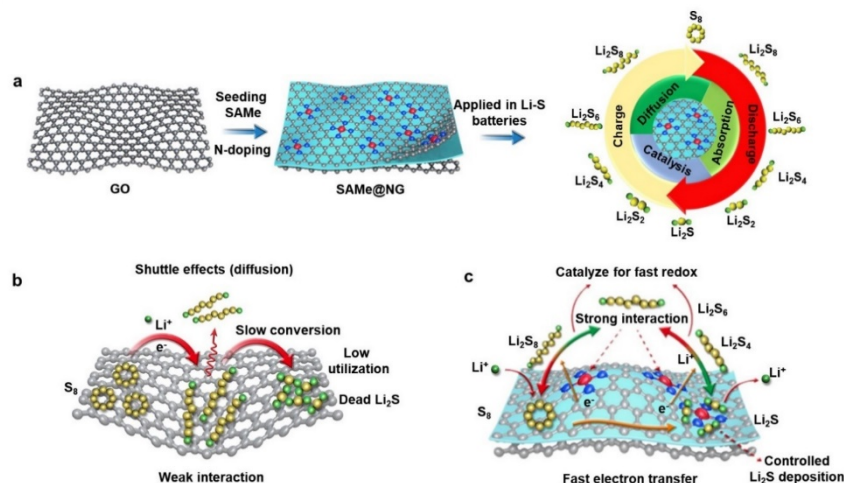
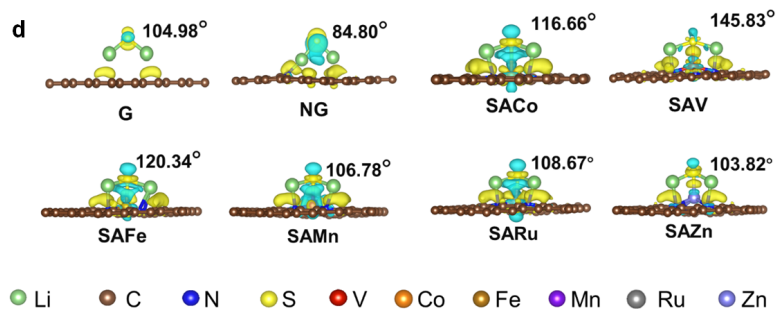
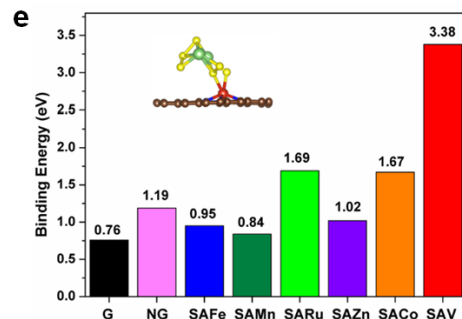
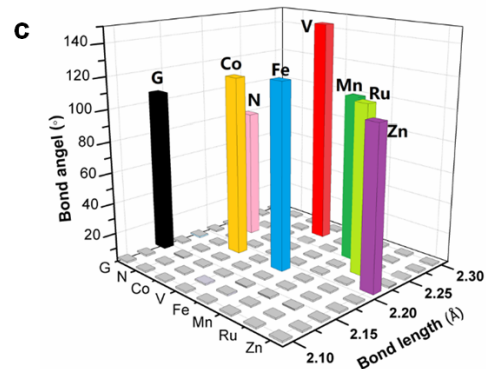
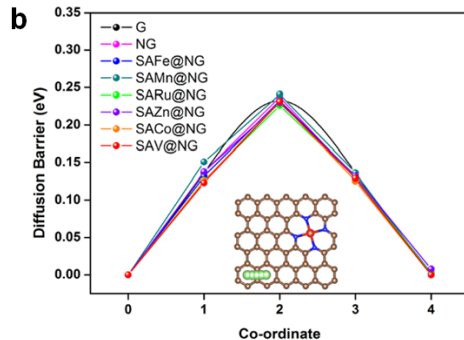
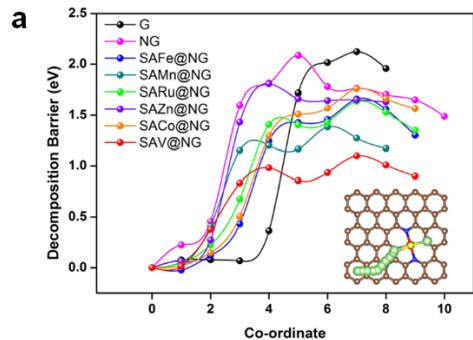
Accomplishment

Electroless deposition of Ni on Melamine foam



Accomplishment

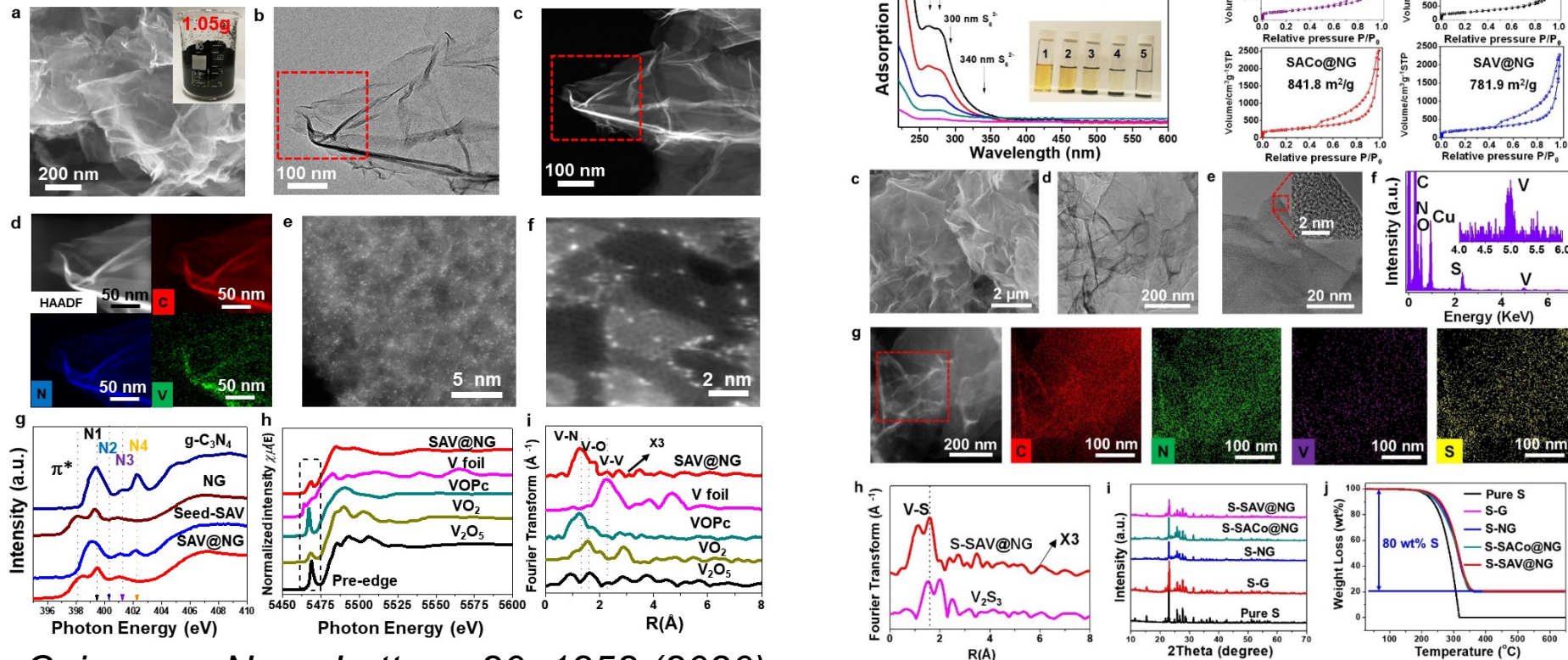
Theoretical understanding for Li_2S decomposition, Li ion diffusion and anchoring effect



Cui group, Nano Letters, 20, 1252 (2020)

Accomplishment

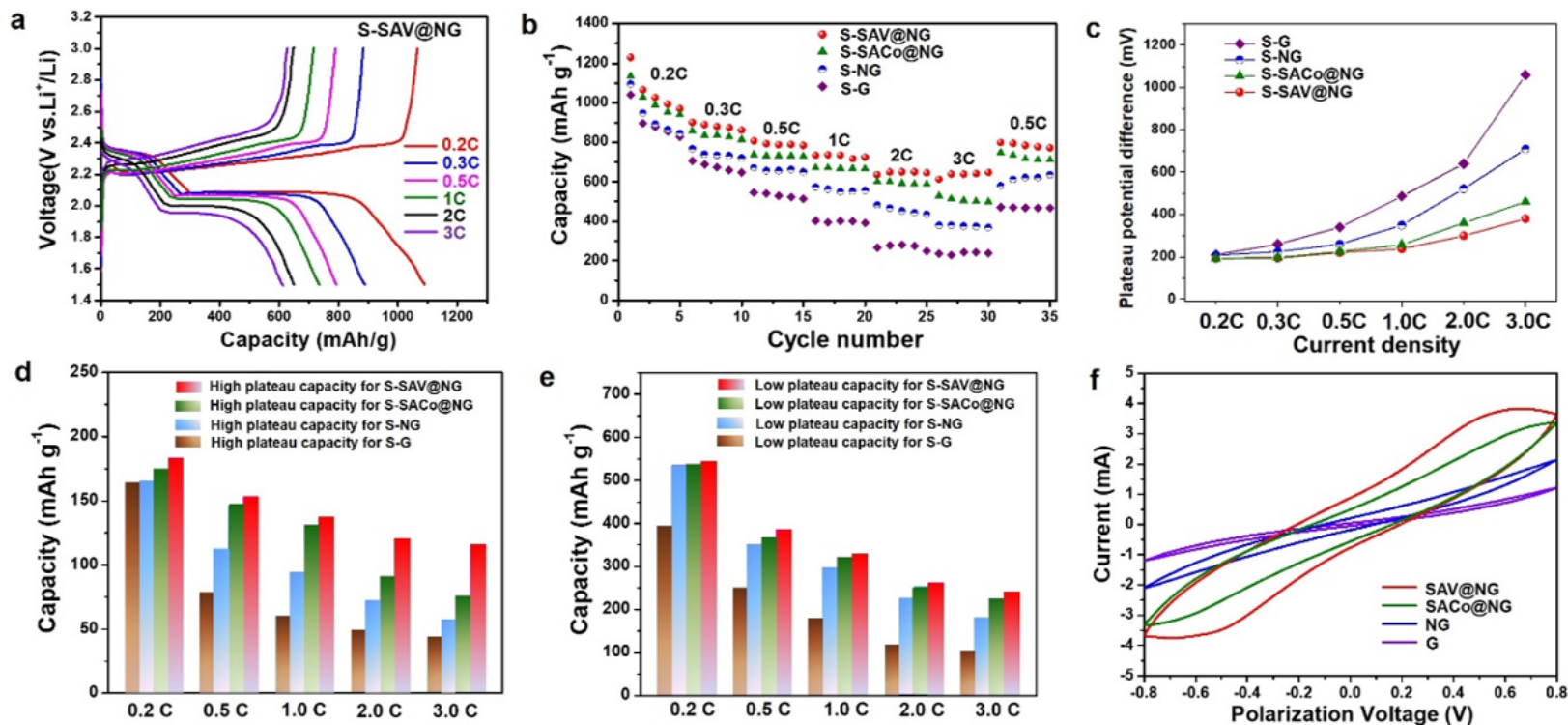
Structural characterizations of SAV@NG



Cui group, Nano Letters, 20, 1252 (2020)

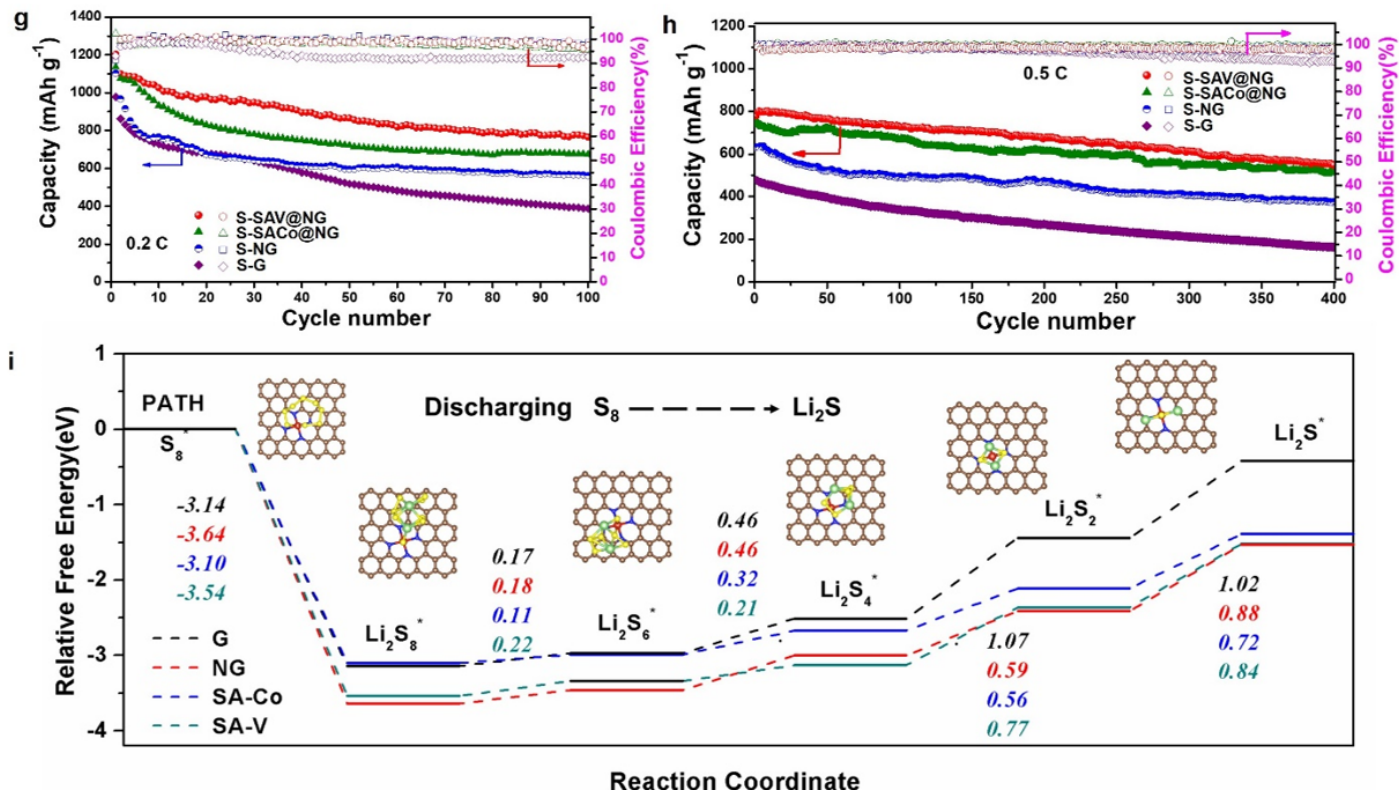
Accomplishment

Electrochemical performance



Accomplishment

Electrochemical performance and mechanism understanding



Responses to Previous Year Reviewers' Comments

None.

Collaboration and Coordination

Stanford University:

- Prof. Steven Chu
- Prof. Zhenan Bao

SLAC:

In-situ X-ray, Prof. Mike Toney

PNNL:

- Dr. Jun Liu
- Dr. Jie Xiao

Remaining Challenges and Barriers

- It is difficult to maintain high capacity and excellent cycling stability of lithium-sulfur batteries while increasing the mass loading of active sulfur in the cathode.
- It is challenging to improve the rate capability (performance of battery at high current densities) of lithium-sulfur batteries.
- It is difficult to fully prevent all the active sulfur species from diffusing into the electrolyte.
- The volumetric energy density of lithium-sulfur batteries needs to be further increased.
- The lithium dendrites grown on the lithium metal surface is a concern for the safety of lithium-sulfur batteries that use lithium metal as anodes.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity sulfur cathodes from the perspective of nanomaterials design to enable high energy lithium-sulfur batteries to power electric vehicles, highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanomaterials synthesis, characterization, battery assembly and testing, and guided by theoretical calculations, which have been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in lithium-sulfur batteries, using rational materials design, synthesizing and testing, and developing scalable and low-cost methods. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational and exciting future has been planned.

Proposed Future Work

- To develop space efficiently packed nanostructured sulfur cathode to increase the volumetric energy density.
- To improve the interparticle contact and conductivity of sulfur nanostructures to increase the kinetics and thus improve the rate capability.
- To test sulfur cathodes with high areal mass loading up to 5 mg/cm² at high current densities.
- To develop approaches to prevent the lithium dendrites growth on lithium metal anodes in lithium-sulfur batteries
- To combine lithium sulfide cathodes with non-lithium anodes, such as silicon, to assemble full batteries to eliminate the safety concern of using lithium metal.
- To develop high performance lithium-sulfur batteries under lean electrolyte.